Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 576–579

Bis(μ-2,2,6,6,10,10-hexamethyl-4,8-dioxaundecanedioato-O^1,O^{11}:$O^{1'}$,$O^{11'}$)bis(pyridine-*N*)dirhodium(II)(*Rh—Rh*)

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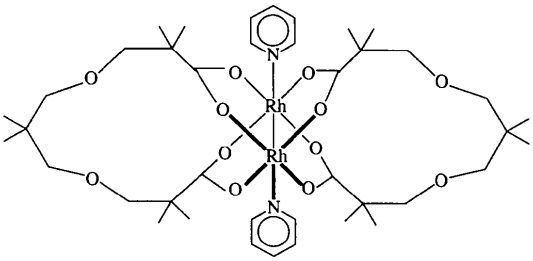
(*Received 4 December 1996; accepted 27 January 1997*)

Abstract

The title compound, $[Rh_2(C_{15}H_{26}O_6)_2(C_5H_5N)_2]$, lies about an inversion centre which is at the midpoint of the Rh—Rh bond. The polyether dicarboxylate ligands bridge the Rh atoms and function as macrocyclic chelates to the Rh—Rh unit. A pyridine molecule is axially coordinated to each Rh atom completing the octahedral coordination. Main dimensions are Rh—Rh 2.4017 (2), Rh—O 2.0367 (9)–2.0405 (9), Rh—N 2.2540 (11) Å and Rh—Rh—N 178.59 (3)°.

Comment

The chemistry of metal–metal bonded complexes has been extensively studied over the past thirty years with the main emphasis largely on individual dinuclear M_2 species (Cotton & Walton, 1994). Recent developments have concentrated on the macromolecular chemistry of M_2 compounds due to the interesting physical properties which may arise from cooperative interaction between the metal centres (Cayton, Chisholm, Huffman & Lobkovsky, 1991; Mashima, Nakano & Nakamura, 1996). Studies on dirhodium(II) complexes have focused on catalysis (Doyle, Kalinin & Ene, 1996; Kennedy, McKervey, Maguire & Roos, 1990) and on rhodium-binding modes in DNA studies (Dunbar, Matonic, Saharan, Crawford & Christou, 1994). We are currently studying dicarboxylic acids (Ferguson, Gallagher & McAlees, 1995) and their reactivity towards metal complexes with a view to exploring applications in catalysis and antitumour chemistry, and report here on the structure and stereochemistry of the title compound, (I).



(I)

Molecule (I) resides on an inversion centre which is at the midpoint of the Rh—Rh bond. The relatively flexible dicarboxylate ligand functions as a macrocyclic chelate to the Rh—Rh unit and adopts two conformations [occupancies 0.943 (3) and 0.057 (3)] in the crystal (see details in the *Experimental* section). The Rh—Rh bond is 2.4017 (2) Å and the carboxylate groups of each dicarboxylate ligand bridge the Rh_2 unit in an orthogonal fashion; the angle between the Rh1, Rh1^i, O11, O12, C1 and Rh1, Rh1^i, O21, O22, C11 planes is 87.36 (3)° [symmetry code: (i) $1-x, -y, -z$]. The Rh—O distances are in the range 2.0367 (9)–2.0405 (9) Å and the *cis*-O—Rh—O angles 87.73 (4)–92.59 (4)°, with Rh—Rh—O 86.82 (3)–88.92 (3)°. A pyridine molecule is axially coordinated to each Rh atom completing the octahedral coordination [Rh—N 2.2540 (11) Å and Rh—Rh—N 178.59 (3)°]. The pyridine ring is bent away from the Rh—Rh—N axis such that atom Rh1 lies 0.282 (3) Å from the plane of the pyridine ring.

In (I), the overall dicarboxylate ligand conformation is determined primarily by the *cis* arrangement of the carboxylate groups. The C—C—C—O torsion angles of the major component of the macrocycle chain (Table 2) all have values close to *gauche* and three of the C—C—O—C torsion angles are close to fully *trans* values;

only the C7—O8—C9—C10 angle [−145.2 (2)°] shows a major distortion from the normal *trans* value. The corresponding torsion angles for the minor component show much more variation with C—C—C—O −68 (1), 87 (2), 95 (1) and −172 (1)°, and C—C—O—C −81 (1), 139 (1), −146 (1) and −153 (1)°. Examination of the structure with *PLATON* (Spek, 1996*a*) showed that there are no solvent accessible voids in the lattice and any potential cavity in the macrocycle generated in (I) is filled by molecular-packing processes. The structure of the parent 2,2,6,6,10,10-hexamethyl-4,8-dioxaundecanedioic acid ligand has been reported (Ferguson, Gallagher & McAlees, 1995) and consists of 'rectangular-shaped' centrosymmetric dimers with any potential central cavity minimized.

There have been several reports on the crystal structures of dirhodium(II) complexes (Mehmet & Tocher, 1991; Cotton & Walton, 1994). Molecule (I) can be compared with $Rh_2(O_2CC_6H_5)_4{:}(C_5H_5N)_2$ [Mehmet & Tocher, 1991; Rh—Rh 2.402 (1) Å and Rh—Rh—N 177.0 (1)°]. There has been only one previous report of a bridged dicarboxylate dirhodium(II) complex and this has an *m*-benzenedipropanoate ligand chelating an Rh_2 unit in a similar fashion to that observed in (I), with Rh—Rh 2.397 Å (Taber, Meagley, Louey & Rheingold, 1995).

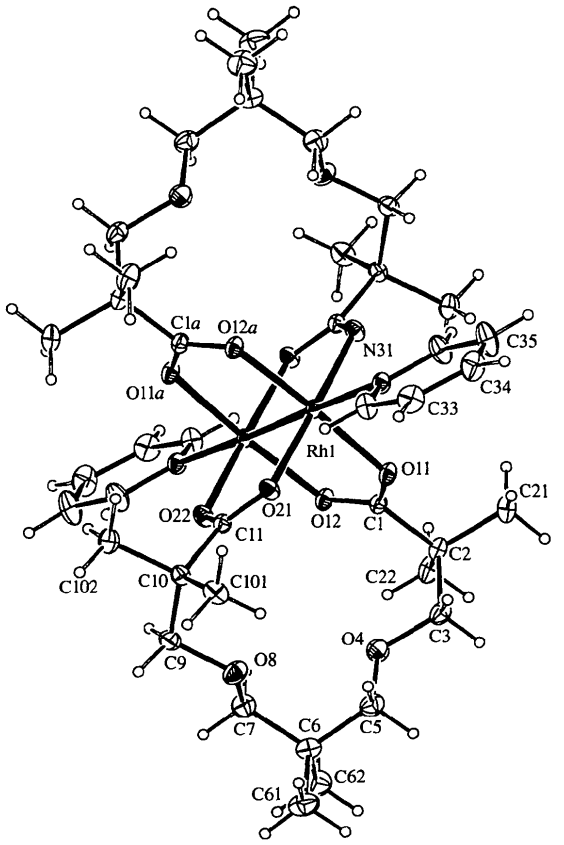


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

Experimental

Following the method of Roos & McKervey (1992), a mixture of $Na_4Rh_2(CO_3)_4.2.5MeOH$ (0.1 mmol) and the dicarboxylic acid (0.4 mmol) in water (10 ml) was heated on a steam bath with stirring for 30 min. The resulting green mixture was allowed to cool and then extracted with CH_2Cl_2 (3 × 20 ml). The combined green extracts were dried using Na_2SO_4, filtered and treated with a few drops of pyridine. An immediate colour change to pink–red was observed and the resulting solution was evaporated to leave a pink–red solid. Crystals suitable for single-crystal X-ray diffraction were grown from benzene containing a drop of pyridine. ^{1}H NMR data (δ, $CDCl_3$): 0.75 (*s*), 0.86 (*s*), 2.90 (*s*), 3.21 (*s*), 7.59 (*m*), 7.95 (*m*), 9.18 (*m*); peak ratios 6:12:4:4:2:1:2. $^{13}C\{^1H\}$ NMR data (δ, $CDCl_3$): 22.16, 23.08, 35.85, 44.81, 77.05 78.06, 124.25, 136.39, 150.99, 195.89.

Crystal data

$[Rh_2(C_{15}H_{26}O_6)_2(C_5H_5N)_2]$
M_r = 968.74
Triclinic
$P\bar{1}$
a = 10.4657 (6) Å
b = 10.8221 (5) Å
c = 11.4160 (5) Å
α = 76.542 (4)°
β = 65.033 (4)°
γ = 73.103 (4)°
V = 1112.5 (1) Å^3
Z = 1
D_x = 1.446 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 16.65–19.85°
μ = 0.801 mm^{-1}
T = 294 (1) K
Block
0.40 × 0.35 × 0.22 mm
Pink–red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.763, T_{max} = 0.838
6464 measured reflections
6464 independent reflections

5634 reflections with $I > 2\sigma(I)$
θ_{max} = 29.9°
h = −13 → 14
k = 0 → 15
l = −15 → 16
3 standard reflections
frequency: 40 min
intensity variation: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0195
$wR(F^2)$ = 0.0462
S = 1.028
6464 reflections
306 parameters
H atoms riding (C—H 0.93–0.97 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 0.2432P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.003
$\Delta\rho_{max}$ = 0.315 e Å^{-3}
$\Delta\rho_{min}$ = −0.401 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0026 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Rh1	0.52980 (1)	0.08756 (1)	0.02450 (1)	0.02623 (3)
O11	0.31949 (10)	0.18279 (9)	0.06832 (10)	0.0370 (2)
O12	0.26204 (10)	0.01676 (9)	0.02738 (10)	0.0357 (2)
O21	0.58051 (11)	0.16705 (9)	−0.16542 (9)	0.0355 (2)
O22	0.52637 (11)	0.00210 (9)	−0.21159 (9)	0.0353 (2)
C1	0.23110 (14)	0.12692 (12)	0.06334 (13)	0.0313 (2)
C2†	0.0744 (2)	0.2031 (2)	0.1048 (2)	0.0368 (6)
C21†	0.0334 (2)	0.2611 (2)	0.2302 (2)	0.0513 (6)
C22†	−0.0300 (2)	0.1188 (2)	0.1259 (3)	0.0531 (5)
C3†	0.0674 (2)	0.3159 (2)	−0.0024 (2)	0.0429 (4)
O4†	0.1083 (2)	0.26649 (12)	−0.12100 (13)	0.0520 (4)
C5†	0.1250 (2)	0.3645 (2)	−0.2288 (2)	0.0502 (4)
C6†	0.1481 (2)	0.3093 (2)	−0.3488 (2)	0.0467 (5)
C61†	0.1731 (2)	0.4193 (2)	−0.4626 (2)	0.0673 (6)
C62†	0.0147 (3)	0.2614 (3)	−0.3276 (3)	0.0678 (8)
C7†	0.2777 (2)	0.1960 (2)	−0.3791 (2)	0.0491 (4)
O8†	0.4025 (2)	0.23639 (13)	−0.3974 (2)	0.0515 (4)
C9†	0.5338 (2)	0.1449 (2)	−0.4480 (2)	0.0419 (4)
C10†	0.6364 (2)	0.1526 (2)	−0.38832 (14)	0.0340 (5)
C101†	0.6590 (4)	0.2910 (2)	−0.4151 (2)	0.0476 (8)
C102†	0.7812 (2)	0.0568 (4)	−0.4458 (2)	0.0517 (11)
C2*D*‡	0.0753 (6)	0.2049 (11)	0.0957 (10)	0.039 (9)
C21*D*‡	0.0129 (17)	0.239 (2)	0.2350 (10)	0.032 (6)
C22*D*‡	−0.0155 (12)	0.1233 (19)	0.085 (2)	0.032 (6)
C3*D*‡	0.0727 (17)	0.3303 (8)	0.0007 (14)	0.034 (4)
O4*D*‡	0.0443 (10)	0.3109 (15)	−0.1041 (10)	0.032 (3)
C5*D*‡	0.1737 (15)	0.2462 (16)	−0.1959 (12)	0.034 (4)
C6*D*‡	0.1676 (13)	0.2809 (16)	−0.3313 (11)	0.039 (9)
C61*D*‡	0.170 (3)	0.4248 (16)	−0.3790 (16)	0.058 (8)
C62*D*‡	0.0280 (15)	0.256 (4)	−0.325 (2)	0.058 (8)
C7*D*‡	0.2976 (15)	0.1969 (19)	−0.4259 (15)	0.034 (4)
O8*D*‡	0.4259 (13)	0.2334 (16)	−0.4466 (16)	0.032 (3)
C9*D*‡	0.537 (2)	0.120 (2)	−0.4487 (12)	0.034 (4)
C10*D*‡	0.6351 (16)	0.142 (3)	−0.3906 (5)	0.039 (9)
C11*D*‡	0.644 (5)	0.286 (4)	−0.422 (3)	0.06 (2)
C12*D*‡	0.7868 (13)	0.058 (6)	−0.4494 (15)	0.06 (2)
C11	0.57386 (14)	0.10499 (12)	−0.24283 (12)	0.0302 (2)
N31	0.57986 (13)	0.25410 (11)	0.07273 (12)	0.0348 (2)
C32	0.6577 (2)	0.3327 (2)	−0.0195 (2)	0.0455 (3)
C33	0.6756 (2)	0.4452 (2)	0.0040 (2)	0.0550 (4)
C34	0.6111 (2)	0.4771 (2)	0.1280 (2)	0.0614 (5)
C35	0.5349 (3)	0.3939 (2)	0.2250 (2)	0.0704 (6)
C36	0.5207 (2)	0.2845 (2)	0.1929 (2)	0.0540 (4)

† Site occupancy = 0.943 (3). ‡ Site occupancy = 0.057 (3).

Table 2. *Selected geometric parameters (Å, °)*

Rh1—Rh1^i	2.4017 (2)	Rh1—N31	2.2540 (11)
Rh1—O11	2.0368 (9)	O11—C1	1.269 (2)
Rh1—O12^i	2.0405 (9)	O12—C1	1.259 (2)
Rh1—O21	2.0367 (9)	O21—C11	1.262 (2)
Rh1—O22^i	2.0386 (9)	O22—C11	1.265 (2)
O11—Rh1—O21	90.71 (4)	O21—Rh1—N31	91.39 (4)
O11—Rh1—O12^i	175.48 (4)	N31—Rh1—Rh1^i	178.59 (3)
O11—Rh1—N31	90.94 (4)		
C1—C2—C3—O4	61.5 (2)	C5—C6—C7—O8	−57.8 (2)
C2—C3—O4—C5	−171.24 (14)	C6—C7—O8—C9	−169.7 (2)
C3—O4—C5—C6	−172.2 (2)	C7—O8—C9—C10	−145.2 (2)
O4—C5—C6—C7	−57.1 (2)	O8—C9—C10—C11	66.7 (2)

Symmetry code: (i) $1-x, -y, -z$.

It was evident during the penultimate stage of refinement {when $R[F^2 > 2\sigma(F^2)]$ was 0.025} that there was a minor component of disorder associated with the dicarboxylate ligand. Several peaks of 0.5 e Å^{-3} were at chemically reasonable distances from each other and in proximity to the dicarboxylate ligand framework. Coordinates for the 15 atoms in the minor disordered component were generated and for the final refinement cycles, a combination of *DFIX* and *EADP* controls was used in the *SHELXL*93 (Sheldrick, 1993) calculations. The relevant part of the *SHELXL*93 information file (with details of the constraints and restraints used) is included in the CIF for this structure. The atoms of the major conformation were refined with anisotropic displacement parameters and the corresponding sites in the minor component were refined isotropically. The final refined site occupancies are 0.943 (3) and 0.057 (3) for the major and minor conformations, respectively. A view showing both major and minor carboxylate ligand conformations has been deposited (as Fig. 2).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: Patterson heavy-atom method and *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93. Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek, 1996*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF* (Ferguson, 1996).

GF thanks NSERC (Canada) for Research Grants. JFG thanks the Research and Postgraduate Committee of Dublin City University for partial funding (Research Grant No. RC96-SRAF-06JG) of a research visit to the University of Guelph (July–August, 1996).

Lists of atomic coordinates, displacement parameters, structure factors, Fig. 2, part of the *SHELXL*93 instruction file and complete geometry have been deposited with the IUCr (Reference: AB1452). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 579–581

2:1 Complex of *N*,*N*′,*N*″-Trimethylnitrilotriacetamide and $Pb(NO_3)_2$

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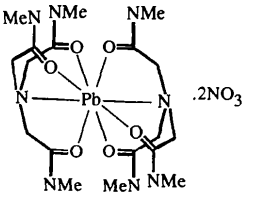
(*Received 4 November 1996; accepted 17 January 1997*)

Abstract

N,*N*′,*N*″-Trimethylnitrilotriacetamide, like underivatized nitrilotriacetamide, forms a 2:1 complex with lead nitrate, namely bis(*N*,*N*′,*N*″-trimethylnitrilo-κN-triacetamide-$\kappa^3 O,O',O''$)lead(II) dinitrate, $[Pb(C_9H_{18}N_4O_3)_2](NO_3)_2$. Increasing the bulk of the organic ligands through methylation of the amide N atoms leads to a reduction in the coordination number of the Pb^{II} atom from ten to nine and eliminates the nitrate anions from the coordination sphere.

Comment

The present report is part of a continuing study of the synthesis (Smith, Sucheck, Cramer & Baker, 1995; Smith, Sucheck, Cramer & Skrzypczak-Jankun, 1992), structure (Skrzypczak-Jankun & Smith, 1994*a*; Skrzypczak-Jankun, Smith & Maluszynska, 1994) and metal-coordinating properties (Skrzypczak-Jankun & Smith, 1994*b*; Smith, Sucheck & Pinkerton, 1992) of novel amide ligands. These compounds are of interest due to their propensity to form intricate hydrogen-bonding networks, their highly polydentate metal-complexing ability, their potential for use in starburst-dendrimer formation and as the materials for toxic waste remediation. This paper describes the three-dimensional structure of the 2:1 complex of *N*,*N*′,*N*″-trimethylnitrilotriacetamide and $Pb^{II}(NO_3)_2$, (I).



(I)

The X-ray analysis has proven (I) to be a nine-coordinate Pb^{II} complex, with the Pb^{II} atom coordinated by six O atoms, one N atom (N17) and the O20′ atom from a symmetry-related molecule forming a distorted cube around the central Pb ion, edge shared with another distorted cube by the center of symmetry through the bridging O20 and O20′ atoms. The other nitrilo N atom (N1) is within bonding distance of the Pb^{II} atom, capping a cube face made by other coordinated atoms. The details of the Pb coordination are given in Table 2.

There are only several other organic ligand complexes of nine-coordinate lead (Herbstein, 1981; Kepert, Patrick, Skelton & White, 1988; Engelhardt, Kepert, Patrick & White, 1989; Byriel *et al.*, 1992; von Arnim, Dehnicke, Maczek & Fenske, 1993). In the previously reported complex of bis(nitrilotriacetamide) [$(ntam)_2$] with lead nitrate (Smith, Sucheck & Pinkerton, 1992), the Pb^{II} atom was ten-coordinate and one of the nitrate groups participated in the coordination. In the title compound, the ligand is the same except that the amide groups of ntam are methylated. The nitrate anions are not bound to the Pb atom. All available N—H groups, together with both nitrate anions, participate in the three-dimensional hydrogen-bonding network (Table 3). The Pb—N distances of 2.848 (4) and 2.783 (4) Å, and the coordination of lead indicate that in this complex, like in $(ntam)_2Pb(NO_3)_2$, the lone electron pair on the Pb atom is also stereochemically inactive.

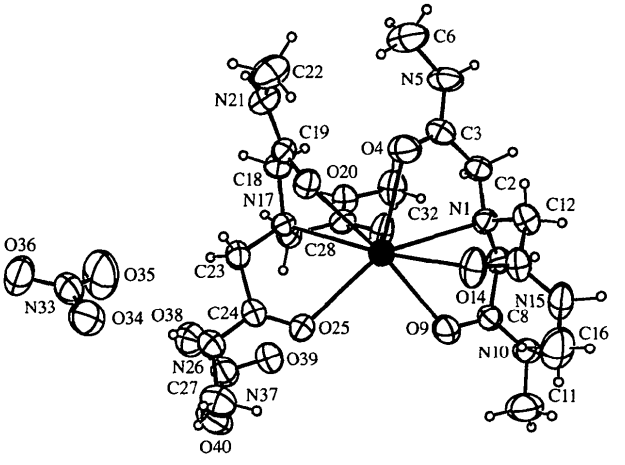


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the title molecule with 50% probability displacement ellipsoids.

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